

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Separation of Liquid Hydrocarbon Mixtures using a Liquefied, normally Gaseous Polar Selective Solvent

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the separation of liquid hydrocarbons mixtures using a liquefied, normally gaseous polar selective solvent.

Various liquefied, normally gaseous polar compounds such as sulphur dioxide and ammonia have been considered over the years for use as selective solvents in the liquid-liquid extraction of certain hydrocarbons streams. Sulphur dioxide, in particular, has been widely used as, for example, for the treatment of light distillates such as heavy naphtha, kerosine and diesel fuel in order to separate aromatics therefrom. The sulphur dioxide process, while generally efficient for the dearomatizing of kerosine and the like to moderate level, i.e., down to 5 percent volume aromatics, is not really suitable for producing products of low aromaticities (aromatic contents) of 1 percent volume or less. In the production of raffinate products of low aromaticities, this process becomes quite expensive due to a rapid increase in solvent requirements. For example, in the processing of kerosine to produce a raffinate having an aromaticity of 3—3.5 percent, the sulphur dioxide solvent is normally employed in a 1:1 ratio to the feed; in order to produce a raffinate product having an aromaticity of 1.2—2.0 percent, the sulphur dioxide solvent to feed ratio is about 2:1; while to produce a material having an aromaticity of about 0.8 percent volume, sulphur dioxide is normally used in a ratio of about 3:1 to the feed. Not only is there a substantial increase in operating cost per volume of charge, but

also the higher solvent requirements in the production of a low aromaticity raffinate substantially reduce the charge throughput of a given plant since these plants are normally designed to be limited as to solvent.

According to the present invention a process for the separation of a liquid hydrocarbon mixture using a liquefied, normally gaseous polar selective solvent comprises separating the mixture into raffinate and extract phases by liquid-liquid extraction with the solvent, contacting at least a part of the raffinate phase with a solid selective adsorbent, and desorbing the adsorbate from the adsorbent with a portion of the liquefied solvent.

Preferably, desorbing solvent is removed from the adsorbent by at least partial vaporization, whereby the adsorbent is made ready for use in treating a further quantity of the extraction raffinate. Vaporization may be effected by a pressure and/or temperature change. The vaporized solvent is suitably liquefied again for re-use in the process.

The process of the invention is particularly suitable for the recovery of polar, especially aromatic, compounds of considerable purity, and/or for the substantially complete removal of aromatics and other materials of similar polarity, e.g., to produce such products, as, for example, odourless kerosine (such as domestic stove oil), transformer oils, white oils and high luminometer number, thermally stable jet fuels (a high luminometer number is an indication of low aromatic content in such fuels).

The two separation procedures of liquid-liquid extraction and adsorption supplement each other in an efficient manner, permitting the operation to take place at optimum performance conditions of each of the separation procedures, with additional advantages from the combination; for adsorption functions at its best with feeds of moderately low aromaticity, whereas liquid-liquid extraction, such

as the sulphur dioxide process, is most efficient at moderate depths of extraction. Thus, in the present process, liquid-liquid extraction is employed initially to remove the aromatics or other polar compounds to a moderate depth, following which the adsorption is used to provide a nearly complete removal of the aromatics or other polar compounds from the raffinate product.

Adsorption using an adsorbent such as silica gel for removing polar compounds such as aromatics is already known per se, e.g., from United States Patent No. 2,564,717. In such a case, benzene and other similar normally liquid materials are used as desorbents for removing the retained polar materials from the adsorbent. Since in this conventional approach the liquid desorbent is in turn displaced from the adsorbent by the polar components in the feed stream, of necessity the desorbent must have approximately the same affinity for the adsorbent as the polar materials which are to be removed. Because of this requisite similarity of desorbent and feed polar components, large quantities of desorbent are required. Since conventionally used desorbents generally do not differ greatly in boiling range from the feed to be treated, the separation and recovery of the desorbent requires extensive fractionation facilities and imposes high heat loads. Moreover, when using a normally liquid desorbent such as benzene the so-called "regenerated" adsorbent is in fact saturated with desorbent, which in turn must be displaced by the polar components of the feed during the subsequent adsorption step. It would be much more efficient if the adsorbent could be actually regenerated, the desorbing material being nearly completely removed from the adsorbent prior to the addition of fresh feed.

In a preferred embodiment of the process according to the invention in which liquefied, normally gaseous solvent is employed both as the extracting solvent in the liquid-liquid extraction and as the desorbing material for the regeneration of the adsorbent, at least substantially complete regeneration is effected by means of at least partial vaporization of the desorbent from the adsorbent after it has served its desorbing function in removing adsorbate therefrom.

Existing installations for sulphur dioxide extraction are readily modified to permit the practice of the present process. In contrast to a conventional process of this kind (not using adsorption) operated to produce a kerosine raffinate of, e.g., less than 1 percent aromatic content, the combined extraction-adsorption process according to the invention supplies a kerosine raffinate at substantially less expense, while permitting about three times the throughput and therefore three times as much product. When the normal

kerosine throughput to the installation is maintained, the sulphur dioxide employed in the liquid-liquid extractor may be reduced to about 70 percent by volume of that normally used, in order to provide the extra quantity of sulphur dioxide required by the adsorption operation. The aromaticity of a kerosine feed may be reduced, for example, from about 22 percent by volume to 5 percent by volume in the extractor, and then from the 5 percent by volume to about 0.8 percent by volume in the adsorption zone. This great reduction in aromatic content is achieved with substantially the same amount of sulphur dioxide as used in conventional operation to produce a product raffinate having an aromaticity of 3—3.5 percent by volume.

A further benefit deriving from the combined process is the possibility of minimizing, and even in some instances eliminating, the costly acid treatment now given to the products of sulphur dioxide extraction, primarily to improve colour. The adsorption treatment of the present process may be used to improve colour at the same time as, or subsequently to, removing aromatics or other polar components.

The liquid, normally gaseous solvent, being highly polar, need be used only in relatively small amounts to desorb or elute the aromatics or other polar compounds from the adsorbent. This is greatly advantageous over the conventional use of large amounts of a liquid desorbent having a polarity close to that of the adsorbate, as previously explained.

The extraction may be carried out in any convenient manner, for example, in mixer-settlers, a packed tower or a rotating disc contactor as described in British patent specification No. 659,241. The adsorption may be carried out cyclically, using one or more fixed beds, or continuously, the adsorbent being circulated. Various adsorbents conventionally used for adsorption, such as silica gel, alumina, silica-alumina cracking catalysts or fluorosilicates are suitable for use in this process.

In the process according to the invention, the hydrocarbon mixture may be passed countercurrently to a stream of liquefied solvent, (e.g., sulphur dioxide) to produce a raffinate of reduced content of more soluble components and an extract phase enriched in such components. The raffinate will contain some solvent, which is suitably removed, e.g., by vaporization in one or more steps. The raffinate is then passed to an adsorption zone where it is contacted with an adsorbent having a strong affinity for the more soluble components (e.g., aromatics) and low affinity for other components (e.g., paraffins). In this latter zone the content of more soluble components of the raffinate is further reduced. In a cyclic process, flow of the extraction raffinate is discontinued when the content of

more soluble components of the adsorption raffinate rises above a predetermined level. Then a stream of liquefied solvent is employed to desorb or elute the adsorbate. The desorbed adsorbate containing solvent may suitably be worked up in a zone, in which solvent is evaporated from the extract, while the raffinate is stripped of its solvent separately, again in one or more steps. Solvent vapours recovered in this way also may be condensed for re-use in the process. The solvent remaining in the adsorption zone after the desorption is recovered. In a preferred embodiment of the process, this recovery is carried out in two (or possibly more) steps. First, the pressure in the adsorption zone is reduced, e.g., to about 5 atm. abs. Most of the solvent is thus removed and can then be liquefied for re-use by cooling with normally available cooling water, which is particularly desirable since it minimizes the requirements for expensive compression facilities. Secondly, the remainder of the desorbent is substantially removed, e.g., by further reduction of the pressure, by increasing the temperature, or by a combination of both.

The invention may be performed in various ways, and a specific embodiment employing a kerosine feed will now be described by way of example with reference to the accompanying drawing which diagrammatically illustrates the apparatus used for performing the process.

Referring to the drawing, the kerosine feed is passed in a line 10 to a liquid-liquid extractor 11, which may be of any suitable design. The feed passes in counter-current flow to a stream of liquefied sulphur dioxide supplied to the extractor by a line 12. Feed and solvent temperatures are adjusted as required by heat exchangers 13 and 14, respectively. In the extraction zone the aromaticity of the raffinate product is reduced to about 5 percent by volume. This raffinate is removed from the extractor in a line 17 and passed to a solvent recovery system 18, in this case comprising flashers and multiple-effect evaporators (not shown). Also, an extract phase from the extraction zone is passed to the recovery system in a line 16. The raffinate and extract are separately stripped of solvent. Generally speaking, both are stripped at similar conditions, with pressures that suitably are from 10.5 atm. to 25 mm. Hg. and temperatures in the range of 10–95° C. Depending upon its pressure, the stripped solvent is either passed directly through a line 19, liquefied in a condenser 20 and sent to a liquefiable gas reservoir 21, or first put through a series of low-pressure compressors. The liquid SO₂ condensate is advantageously at a temperature of approximately 30° C. and a pressure of 5 atm. upon

its removal from condenser 20.

During adsorption, an at least substantially SO₂-free raffinate from the last stage of the raffinate evaporator is fed in a line 22 through a valve 23 to an adsorption system 24. The preferred temperature of the raffinate is 65–70° C., although generally speaking, it can be in the range of from ambient temperature to 95° C. Low-aromatic raffinate product flows out through a valve 26 in a line 27 to a stripper 28. Recovered sulphur dioxide is returned in a line 29 to the solvent recovery system 18 for compression and/or condensation and the finished raffinate product is withdrawn in a line 31.

When the adsorption phase is completed valve 23 is closed and SO₂ is introduced from reservoir 21 via line 32 and valve 33. The solvent is maintained in liquid phase by appropriate regulation of the outlet valves 26 and 34 to keep sufficient pressure on the system. The first portion of the liquid SO₂ supplied during desorption displaces the interstitial volume of raffinate material remaining from the adsorption step. Part of this material is removed in line 27 as raffinate and the remainder, along with the desorbed aromatics in SO₂, is sent to the solvent recovery system 18 through valve 34 and line 36. The extract products recovered from extraction and from adsorption are removed via line 37.

Following removal of the aromatic adsorbate a major portion of the remaining SO₂ is removed from the system in line 38 by slowly reducing the pressure, suitably to about 5 atm. abs., by appropriate adjustment of valve 39. Because of its pressure, the sulphur dioxide liberated in this manner can be liquefied with cooling water in condenser 20 without prior compression. In a preferred method of operation the regeneration is completed by further reducing the system pressure to around atmospheric or lower. However, substantially the same effect can be obtained by heating the adsorbent to about 100° C. at 5 atm. abs., or by using a combination of pressure reduction and heating. The regeneration may be considered complete when the SO₂ concentration on the adsorbent has been reduced to about 5 percent weight. At this point the adsorbent is in condition to adsorb aromatics from an additional quantity of extraction raffinate.

The invention is further illustrated by means of the following Examples.

EXAMPLE I

A kerosine feed containing about 22 percent by volume of aromatics is worked up in a manner as explained above with reference to the drawing, using SO₂ as the solvent. The results obtained are represented in Table I.

TABLE I

	Extraction	Adsorption	Overall
Feed quantity, l/day	350,000	286,000	350,000
Feed aromatics content, % v/v	22	5	22
Solvent, l/day	238,000	112,000	350,000
Raffinate quantity, l/day	350,000	262,000	262,000
Raffinate aromatics content, % v/v	5	0.8	0.8
Extract quantity, l/day	63,500	23,800	87,500
Raffinate yields, based on feed, % v/v	~82	~92	~75

EXAMPLE II

Aromatics and other undesirable petroleum constituents were removed from a catalytically cracked heavy naphtha containing about 33 percent paraffins and naphthenes, 19 percent olefins, and 48 percent aromatics using liquefied ammonia. The naphtha was fed to a multiple stage extraction tower operated at between 5 and 65° C. at such a pressure as to ensure that the solvent (which may be pure ammonia or ammonia fortified with mono-methylamine or other similar compounds) remains in a liquid state. Reflux may be generated by imposing a temperature gradient across the extraction column or by adding a precipitant or anti-solvent such as water. Dependent upon the number of stages in the extraction unit, the solvent used and the temperature gradient imposed, if any, the separation of aromatics from paraffins and naphthenes may be more or less complete. Thus, extracts containing 90 percent aromatics and 6 percent olefins, or 78 percent aromatics and 12 percent olefins, may be obtained with corresponding raffinates containing 24 percent olefins, 75 percent paraffins and naphthenes and 1 percent aromatics, or 18 percent olefins, 50 percent paraffins and naphthenes and 32 percent aromatics, respectively. In the case of the substantially complete removal of aromatics from the raffinate, the subsequent adsorption primarily serves to remove undesirable colour bodies, diaromatics or other undesirable polar constituents. Under more normal operation, where 2 to 10 percent aromatics remain in the raffinate, the adsorption is mainly used to further remove aromatics.

The raffinate from the solvent extraction is then fed at 10 to 50° C. on to silica gel, from which nearly all the ammonia used during the previous cycle has been removed. The vapour pressure in the column is at or near atmospheric and the feed rate suitable for the viscosity and temperature of the feed. When the raffinate issuing from the column has reached the maximum content of

adsorbate permissible for the desired product, the product is switched from a raffinate receiver to a recycle receiver. Depending upon the quality and yield of extract desired the recycle stream may be adjusted as required; a large recycle stream gives raffinates and extracts of high purity but recycling is time consuming and reduces the throughput of a unit.

The desorbing solvent is then fed to the silica gel during such a time as will permit the production of the desired quality of raffinate or recycle stream. The column is operated with sufficient pressure to avoid vaporization of the ammonia at maximum column temperature. When the liquid ammonia has removed the adsorbate, the introduction of ammonia to the column is stopped and most of the liquid ammonia is forced from the column by slightly reducing the pressure and letting ammonia gas force out liquid ammonia.

When at least substantially all liquid ammonia has been removed from the column, ammonia gas is then removed by reducing the pressure to atmospheric or less. As ammonia is very tightly adsorbed to silica gel, elevated temperatures may be required to remove the ammonia from the gel. The column may be heated externally, e.g., with steam, to from 95—185° C. to remove the ammonia. After the gel has had time to come to equilibrium at this temperature, it is ready for cooling prior to a new feed cycle. When the gel has a temperature of 10—85° C., the feed cycle may be resumed.

The solvent extraction and adsorption units may use conventional solvent recovery systems as indicated above with reference to a process using sulphur dioxide.

WHAT WE CLAIM IS:—

1. A process for the separation of a liquid hydrocarbon mixture using a liquefied normally gaseous polar selective solvent, which comprises separating the mixture into raffinate and extract phases by liquid-liquid

extraction with the solvent, contacting at least a part of the raffinate phase with a solid selective adsorbent, and desorbing the adsorbate from the adsorbent with a portion of the liquefied solvent.

2. A process as claimed in Claim 1 in which the adsorbent is selective for at least part of the components more soluble in the solvent.

3. A process as claimed in Claim 1 or Claim 2 in which interstitial raffinate material remaining in the adsorbent after adsorption is removed by contacting with a portion of the liquefied solvent.

4. A process as claimed in Claim 1 or Claim 2 or Claim 3 which includes removing solvent from the adsorbent by at least partial vaporization.

5. A process as claimed in Claim 4 in which the solvent concentration on the adsorbent after solvent removal is about 5% by weight.

6. A process as claimed in Claim 4 or Claim 5 which includes carrying out the solvent removal from the adsorbent in two or more steps of decreasing pressure.

7. A process as claimed in Claim 4 or Claim 5 or Claim 6 which includes carrying out the solvent removal from the adsorbent in two or more steps of increasing temperature.

8. A process as claimed in any of the preceding claims which includes at least substantially removing solvent from the raffinate phase of the extraction which is to be contacted with the adsorbent.

9. A process as claimed in any of the preceding claims which includes condensing for re-use solvent vapours recovered in the process.

10. A process as claimed in any of the

preceding claims in which colour bodies are removed in the adsorption treatment.

11. A process as claimed in any of the preceding claims in which the more soluble components are aromatics and/or other polar components.

12. A process as claimed in any one of the preceding claims in which the hydrocarbon mixture to be separated is a material boiling in the kerosine range.

13. A process as claimed in Claim 12 in which the hydrocarbon mixture contains 20—25% of aromatics by volume.

14. A process as claimed in any of the preceding claims in which the solvent comprises sulphur dioxide.

15. A process as claimed in any of Claims 1 to 13 in which the solvent comprises ammonia.

16. A process as claimed in Claim 15 in which the solvent also contains monomethylamine.

17. A process as claimed in any of the preceding claims in which the adsorbent comprises silica gel.

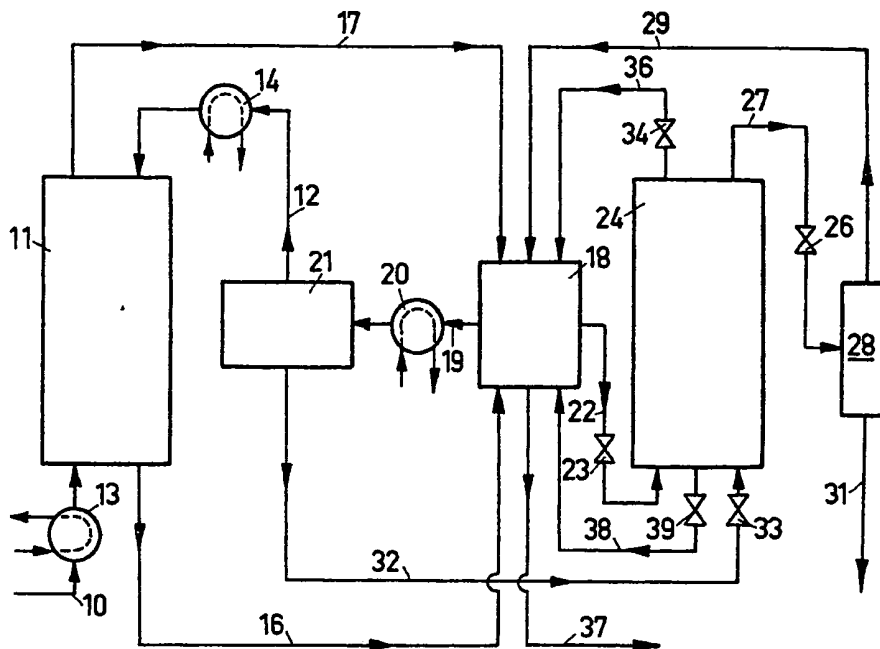
18. A process for the separation of a liquid hydrocarbon mixture using a liquefied normally gaseous polar selective solvent, substantially as described with reference to the accompanying drawing and the Examples.

19. A hydrocarbon mixture of reduced content in aromatics and/or other polar materials obtained using a process as claimed in any of the preceding claims.

20. Aromatics or other polar materials or mixtures comprising them obtained using a process as claimed in any of Claims 1 to 18.

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